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Quantitative prediction of gas-phase ^{13}C NMR chemical shifts

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The accurate prediction of NMR chemical shifts is still a great challenge. While typical errors in SCF ^{13}C chemical shift calculations are about 5-10 ppm, application of correlated methods reduces the errors signifficantly. Nevertheless it has so far not been possible to predict chemical shifts with an accuracy of about 1 ppm or better and thus to reach quantitative accuracy compared to experimental gas phase NMR data.
In this study we demonstrate that this accuracy can be achieved if :

- chemical shifts are calculated at CCSD(T) level using large basis sets, e.g. of pentuple zeta quality augmented by higher angular momentum funcitons,
- employed molecular geometries are taken from CCSD(T) optimizations using sufficiently large basis sets such as cc-pVTZ or cc-pVQZ,
- vibrational corrections to chemical shifts are included.

Calculations of ^{13}C chemical shifts for a set of 15 small organic compounds containing different types of bonding environments are presented. A detailed study of the effects of correlation level, basis set convergence and the need of vibrational corrections is carried out in order to reach a maximum deviation of less than 1 ppm.
The results are compared to experimental gas phase ^{13}C NMR data.

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